RESEARCH PROPOSAL

Synthesis and Application of New Aminated Fe_3O_4 Magnetic Nano-Catalysts

For registration to the degree of Doctor of Philosophy

IN THE FACULTY OF SCIENCE

THE IIS UNIVERSITY, JAIPUR

Submitted by

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under the supervision of

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➢ Introduction

Catalysis plays a central role in chemical transformations and lies at the heart of countless chemical protocols, from academic research at laboratories level to the chemical industry level. By using catalytic reagents, one can reduce the temperature of a transformation, reduce reagent-based waste and enhance the selectivity of a reaction that potentially avoids the unwanted side reactions leading to a green technology. A variety of products, such as medicines, fine chemicals, polymers, fibres, fuels, paints, lubricants, and a myriad of other value added products essential to humans, would not be feasible in the absence of catalysts.

Why do we need nano-catalysis ?

A homogeneous catalyst, where the catalyst is in the same phase as the reactants, is generally accepted by chemists.[1] One attractive property is that all catalytic sites are accessible because the catalyst is generally a soluble metal complex. Furthermore, it is possible to tune the chemo-, regio- and enantioselectivity of the catalyst. Homogeneous catalysts have a number of other advantages such as high selectivities, better yield, and easy optimization of catalytic systems by modification of ligand and metals. They are widely used in a number of commercial applications, but the difficulty of catalyst separation from the final product creates economic and environmental barriers to broadening their scope. Despite their advantages and their wide use in a number of applications, many homogeneous catalytic systems could not be commercialized because of the difficulty encountered in separating the catalyst from the final reaction product.

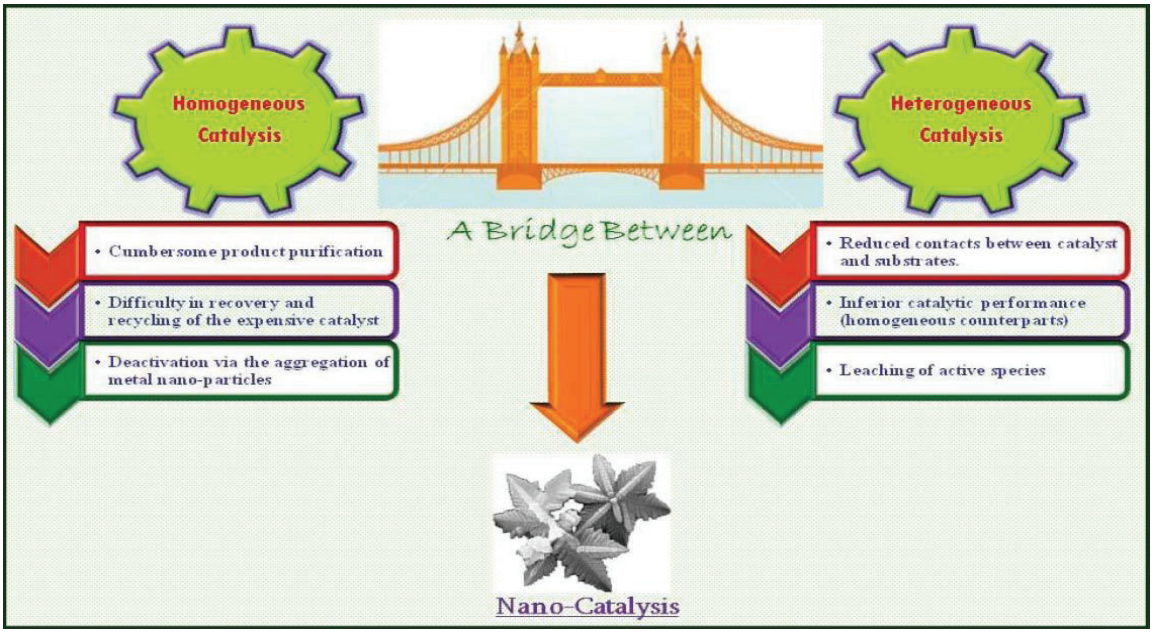

Homogeneous Catalysis
A Bridge Between
Heterogeneous Catalysis
• Cumbersome product purification
• Difficulty in recovery and recycling of the expensive catalyst
• Deactivation via the aggregation of metal nano-particles
• Reduced contacts between catalyst and substrates.
• Inferior catalytic performance (homogeneous counterparts)
• Leaching of active species
Nano-Catalysis

Fig. 1

Efficiency of catalysis :-

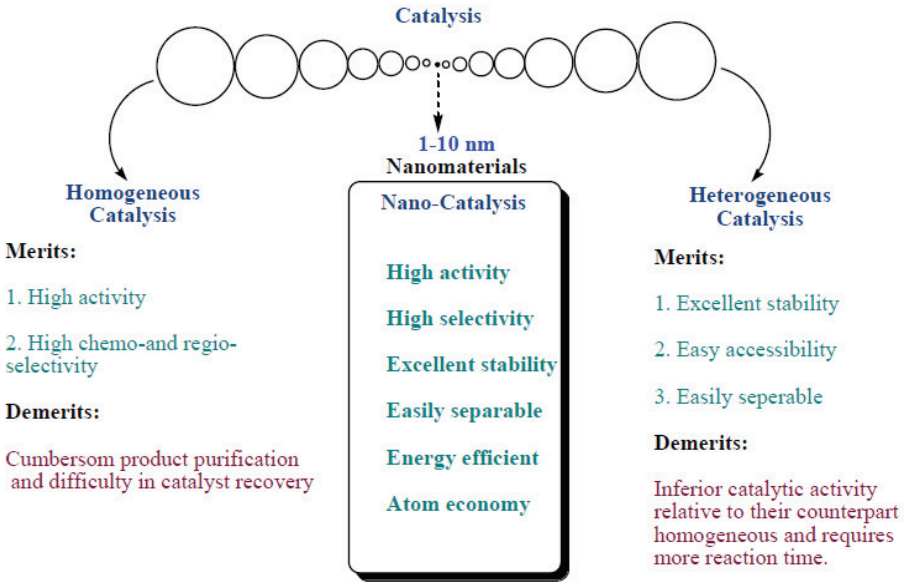


Fig. 2: Comparative efficiency of homogeneous, heterogeneous and nano-catalysis

Among three well-known catalysis categories e.g. homogeneous, heterogeneous and enzymatic catalysis, enzymatic catalysis is the most efficient and greenest catalysis found in nature. Both the homogeneous and heterogeneous catalysis has its own merits and demerits due to which there is urgent need of a new catalytic system, which should be active like homogeneous catalysis, and should also be easily recoverable like heterogeneous catalyst.[2]

Nano-catalysts have combined advantages of both the homogeneous and heterogeneous catalytic systems. Nano catalytic system allows the rapid, selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery. Recovery of catalysts from the system is most important characteristics of any catalyst before being acceptable for green chemical manufacturing processes in industry. Because of nano size (high surface area) the contact between reactants and catalyst increases dramatically (this phenomenon is close to homogeneous catalysis). Insolubility in the reaction solvent makes the catalyst heterogeneous and hence can be separated out easily from the reaction mixture (this phenomenon is close to heterogeneous catalysis).[3-7]

What is nano-catalysis ?

Nanoparticles have emerged as sustainable alternatives to conventional materials, as robust, high surface area heterogeneous catalysts [8] and catalyst supports.[9] The nano-sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts.

However, their insolubility in reaction solvents renders them easily separable from the reaction mixture like heterogeneous catalysts, which in turn makes the product isolation stage effortless. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology (Fig. 3).

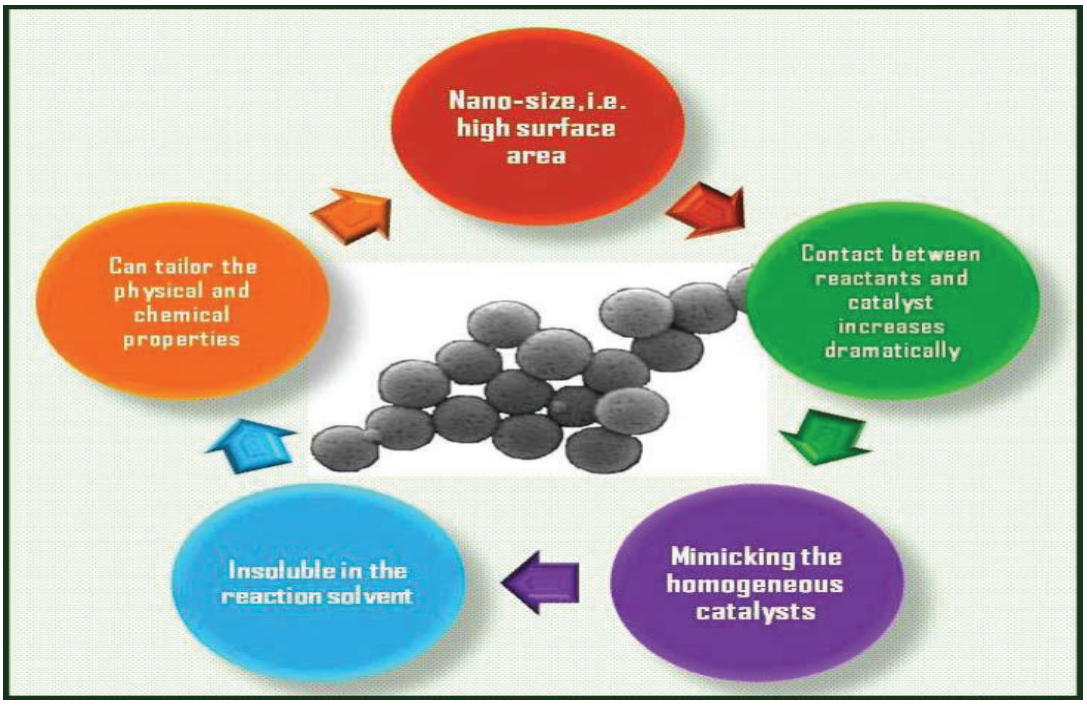

Nano-size,i.e. high surface area
Contact between reactants and catalyst increases dramatically
Mimicking the homogeneous catalysts
Insoluble in the reaction solvent
Can tailor the physical and chemical properties

Fig. 3

The scientific challenge is the synthesis of specific-size and shape nano-catalysts to allow facile movement of materials in the reacting phase and control over morphology of nanostructures to tailor their physical and chemical properties. However, the rapid advancement of nano-technology made possible the preparation of a variety of nanoparticles with controlled size, shape, morphology and composition.[10]

Benefits of nano-catalysis :-

By precisely, controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nano components, it can be widely used in catalysis with newer properties and activity. Nanostructured catalysts have been the subject of considerable academic and industrial attention in recent times due to the numerous potential benefits that can accrue through their use.[11] (Fig. 4).

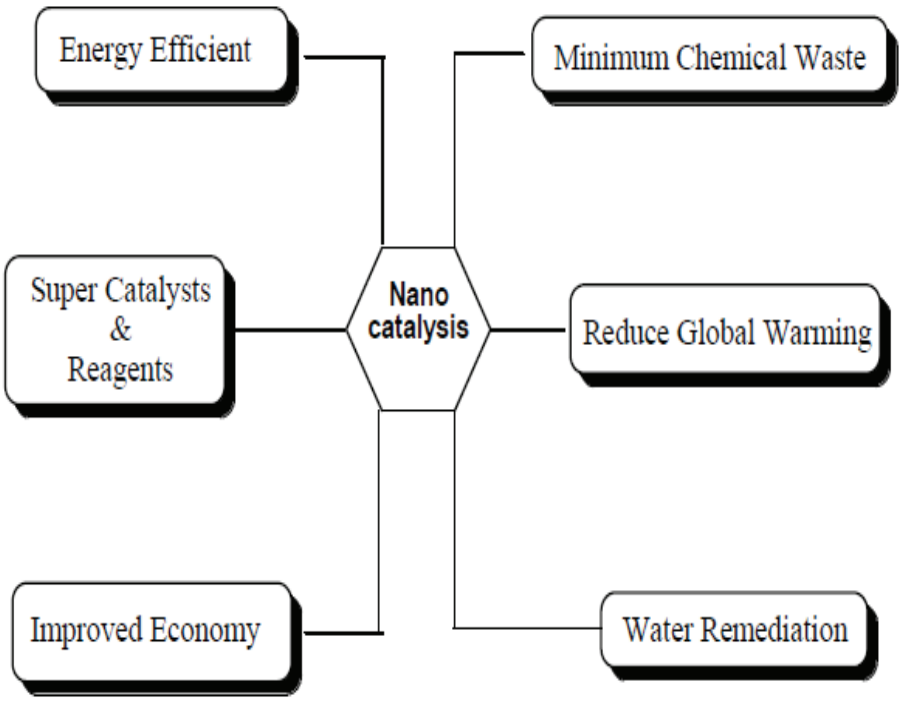


Fig. 4: Benefits of nano-catalysis

Magnetic Nano-catalyst Fe_3O_4 :-

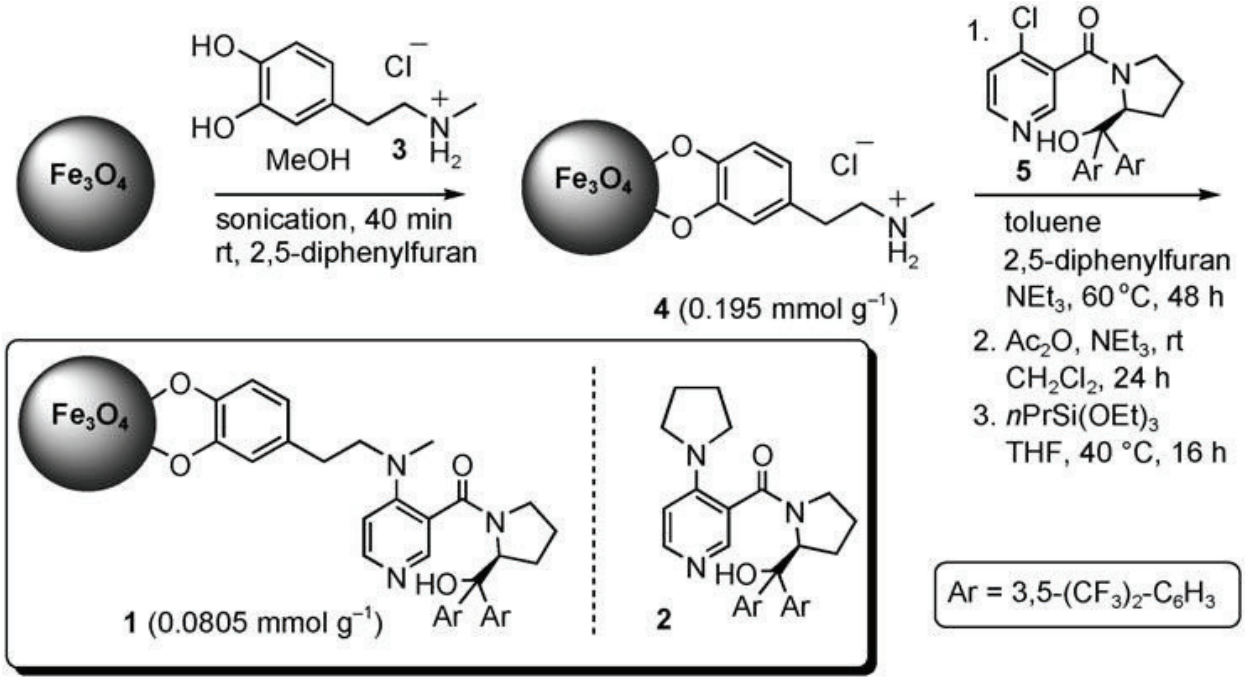
The synthesis of magnetite nanoparticles with controlled size has long been of scientific and technological interest. Magnetite (Fe_3O_4) is a common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming a fcc closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites.[12]

The electrons can hop between Fe^{2+} and Fe^{3+} ions in the octahedral sites at room temperature, rendering magnetite, an important class of half-metallic materials.[13] Its particle dispersions have been widely used as ferrofluid , for example in rotary shaft sealing, oscillation damping, and position sensing.[14] The use of properly coated magnetite nanoparticles in clinical medicine has also intensified. With proper surface coating, these magnetic nanoparticles can be dispersed into water, forming water-based suspensions.[15] Such a suspension can interact with an external magnetic field and be positioned to a specific area, facilitating magnetic resonance imaging for medical diagnosis[16] and AC magnetic field-assisted cancer therapy.[17] All these technological and medical applications require that the nanoparticles are superparamagnetic with sizes smaller than 20 nm and the overall particle size distribution is narrow so that the particles have uniform physical and chemical properties. However, producing magnetite particles with the desired size and acceptable size distribution without particle aggregation has consistently been a problem.

Fe_3O_4 nanoparticles are commonly produced via coprecipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions by a base, usually NaOH, or $NH_3.H_2O$, in an aqueous solution,[18] or they may be made by thermal decomposition of alkaline solution of Fe^{3+} chelate in the presence of hydrazine[19] and by sonochemical decomposition of hydrolysed Fe(II) salt followed by thermal treatment.[20] The disadvantage of these aqueous solution syntheses is that the PH value of the reaction mixture has to be adjusted in both the synthesis and purification steps, and the process toward smaller (<20 nm) monodisperse nanoparticles has only very limited success. Organic solution-phase decomposition of the iron precursor at high temperatures has been widely used in iron oxide nanoparticle synthesis.

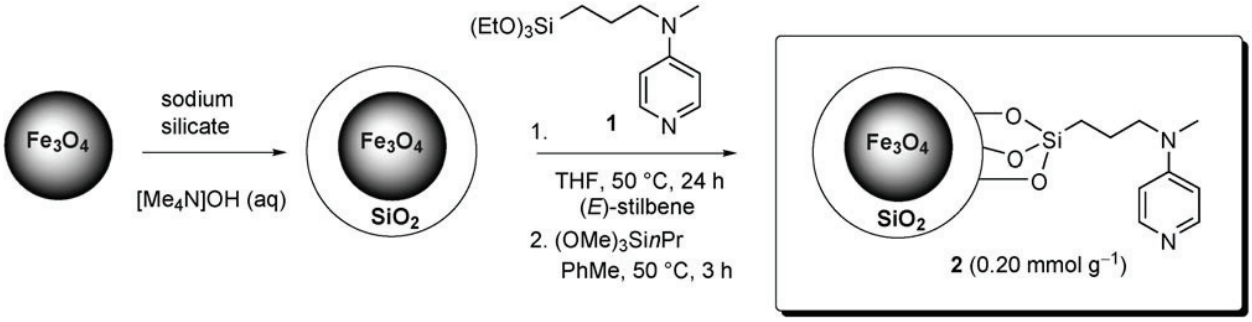
➢ Review of Literature

❖ **Gleeson *et al*.** reported the first magnetic nanoparticle-supported chiral DMAP analogue and found highly enantioselective acylation and excellent recyclability of magnetic nano particle.[21] (Scheme 1)



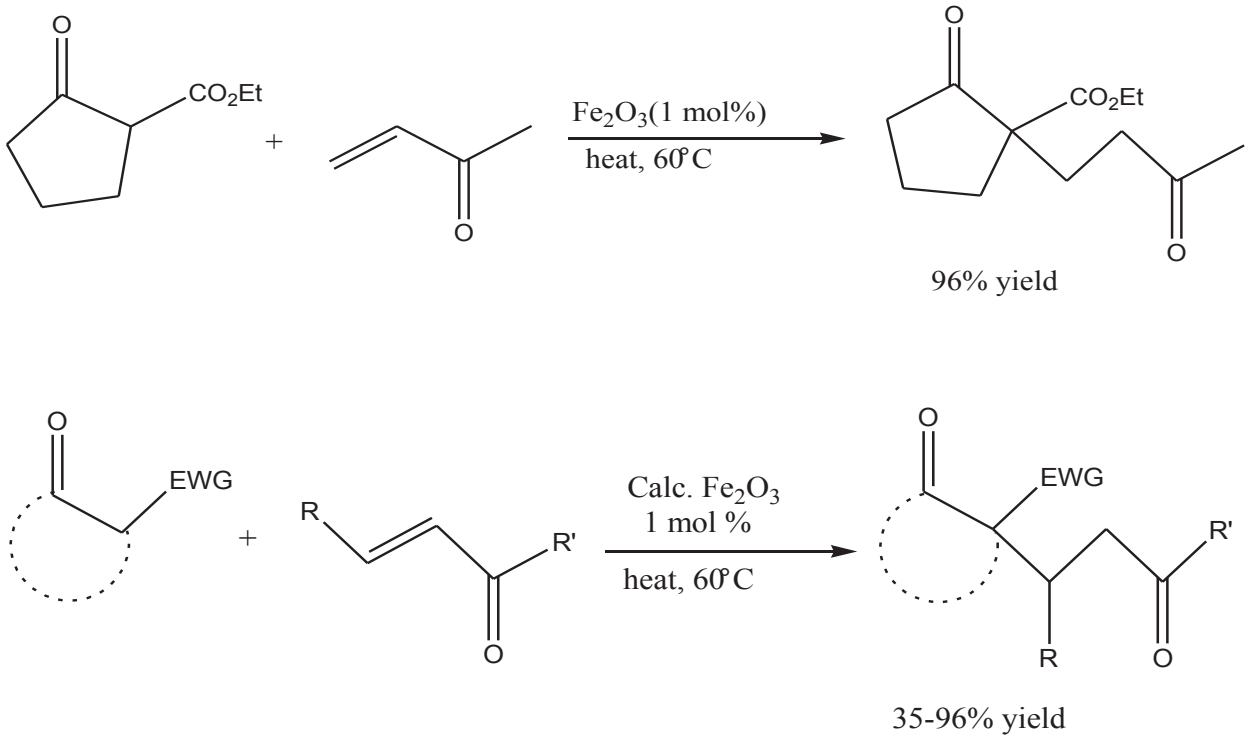
Scheme 1. Synthesis of immobilized catalyst

❖ **Dalaigh *et al*.** reported a magnetic nanoparticle-supported 4-N,N-dialkylaminopyridine catalyst, they found excellent reactivity combined with facile catalyst recovery and recyclability of magnetic nanoparticle.[22](Scheme 2)



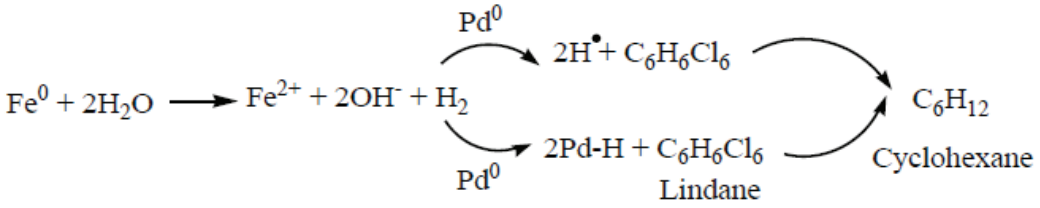
Scheme 2. Synthesis of the magnetic-nanoparticle-supported 4-N,N-dialkylaminopyridine catalyst

❖ **J.Meriam *et al.*** reported Michael addition of 1,3-dicarbonyl compounds catalysed by Iron Oxide nanocatalyst and yield was in good amount.[23] (Scheme 3)



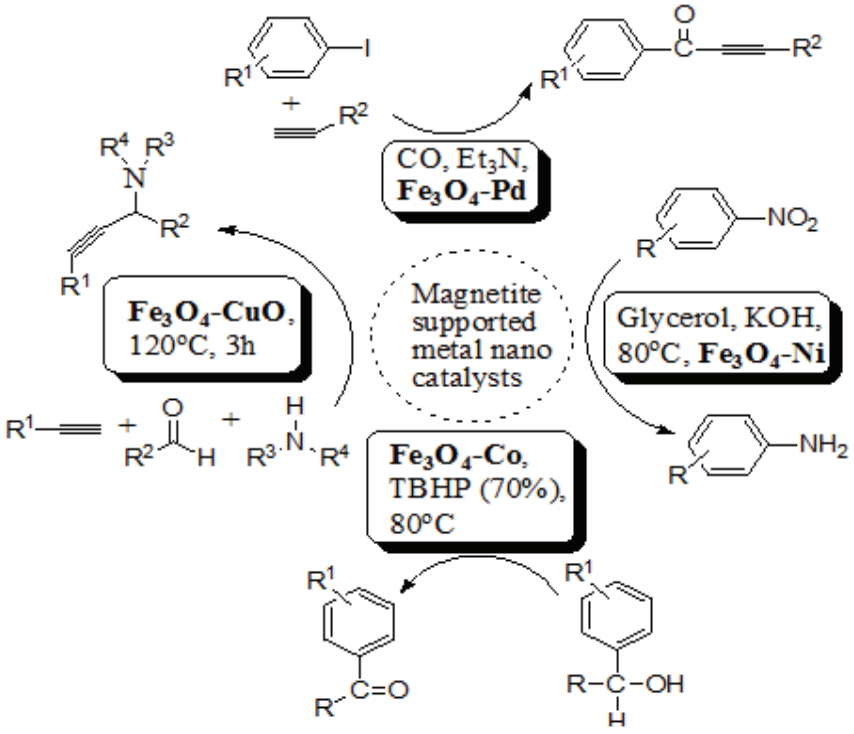
Scheme 3.

❖ **Nagpal *et al.*[24]** reported the reductive dechlorination of lindane (γ-hexachlorocyclohexane) in aqueous medium catalysed by nanoscale Fe-Pd bimetallic particles (Scheme 4). Presence of palladium on the surface of nanoscale iron particles increased the catalytic activity of Fe-Pd bimetallic system to enhance the dechlorination of lindane. Dechlorination occurs via adsorption of chlorinated compounds (lindane) on the particle surface.[25] Palladium on the surface acts as a collector of hydrogen gas that is produced by reduction of water molecule in presence of nanoscale iron (iron corrosion reaction). Nanoscale palladium (Pd0) reacts with hydrogen gas to form either metal hydride or hydrogen radicals. Both are highly reactive towards C–Cl bonds and finally replace the entire chlorine atoms from lindane to form cyclohexane.



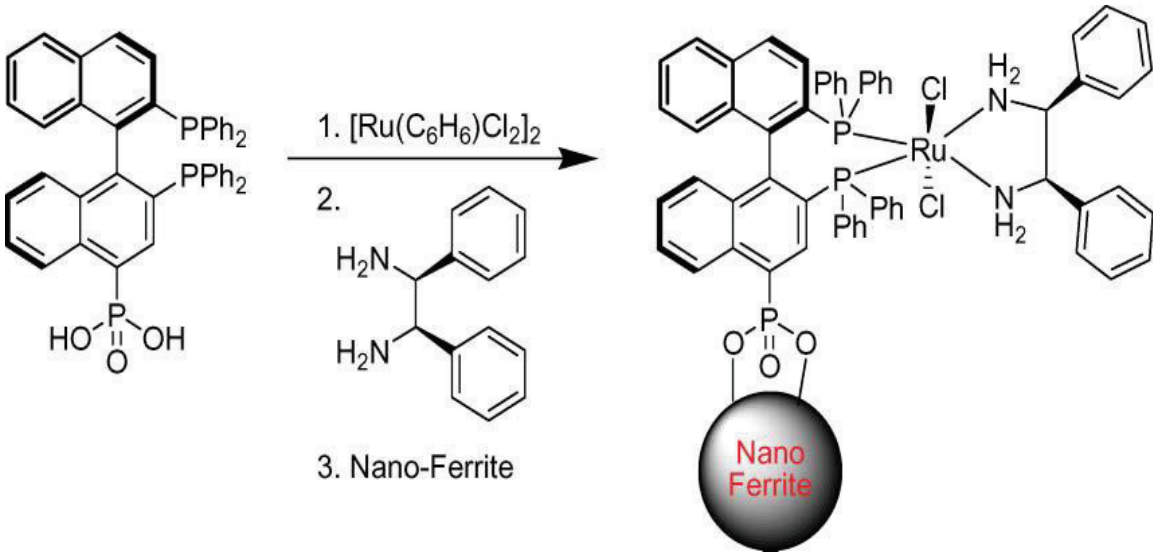
Scheme 4. Nanoscale Fe0-Pd0 bimetallic nanoparticle catalyzed dechlorination of lindane

- **Gawande *et al.*[26]** reported the use of surface functionalized nano-magnetite supported nanoparticles in catalysis, green chemistry and pharmaceutically significant reactions. These nanoparticles act as bridge between heterogeneous and homogeneous catalysis. Magnetite-supported metal nanocatalysts have been successfully used in organic synthesis for a variety of important reactions.[27-30] (Scheme 5).



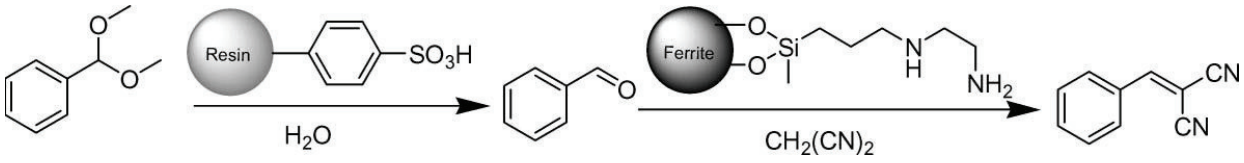
Scheme 5. Magnetic supported metal nanoparticle catalysed some organic reactions

❖ **Lin *et al*.** designed a magnetite nanoparticle-supported chiral catalyst by Ru-complex formation with BINAP followed by functionalization on the ferrite surfaces (Scheme 6). The synthesized material catalyzed the asymmetric hydrogenation of aromatic ketones under heterogeneous conditions with high activity and enantioselectivity. The catalyst could be recovered by using an external magnet and was used up to 14 times without any change in activity.[31]



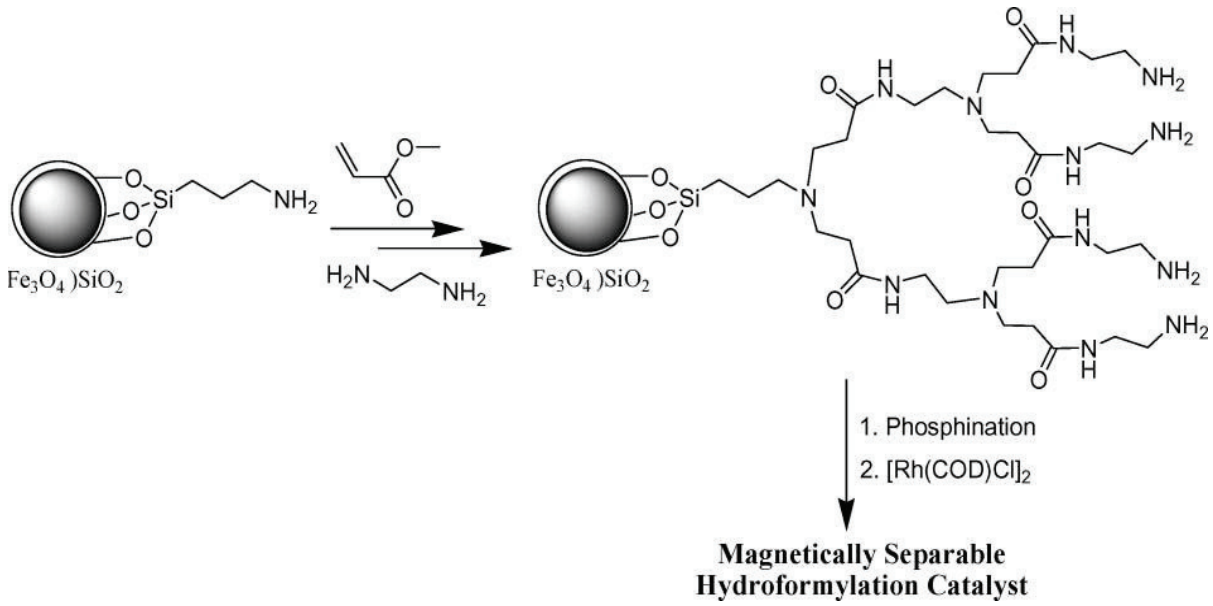
Scheme 6. Synthesis of nanoparticle-supported chiral Ru-catalyst.

❖ The afore mentioned concept of magnetically separable catalysts was also explored by **Jones *et al*.** for a one-pot multistep reaction. They used a polymer resin-based acid catalyst and magnetic ferrite-based base catalyst, for conversion of 1-(dimethoxymethyl)benzene to 2 benzylidenemalononitrile in a two-step single pot reaction (Scheme 7). After completion of the reaction, the resin-based catalyst was removed by decantation and the ferrite-based catalyst was removed by an external magnet, essentially in pure form.[32]



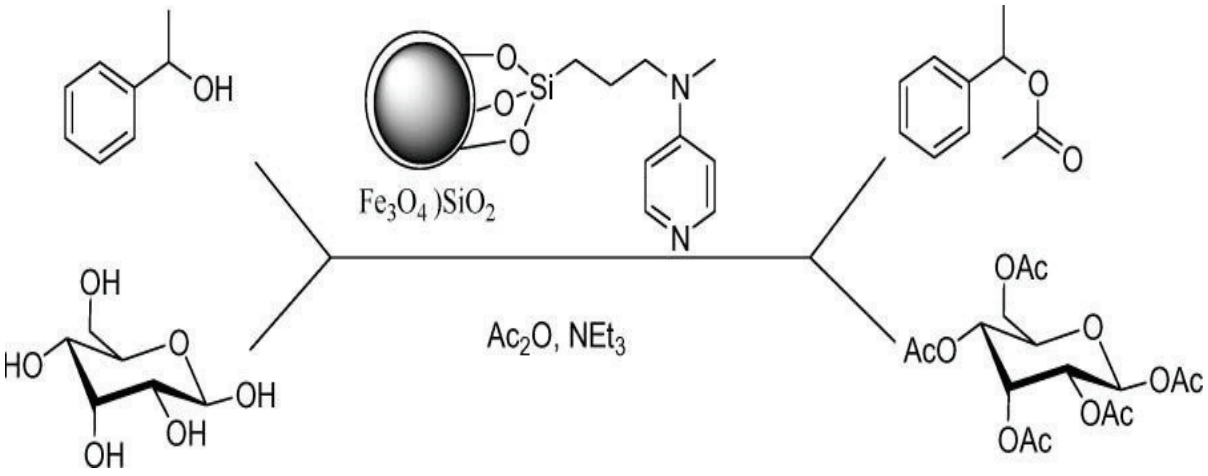
Scheme 7. Synthesis of magnetically separable acid catalyst.

❖ **Alper and his co-workers** developed the method to homogenize these magnetically separable heterogeneous catalysts by growing polyaminoamido dendrons on silica-coated nanoferrites up to three generations, followed by phosphination.[33] The material was then complexed with rhodium and used as a catalyst for a hydroformylation reaction (Scheme 8). The ensuing catalyst was found to be stable and more soluble in organic solvent and catalyzed the reaction with excellent reactivity and selectivity.



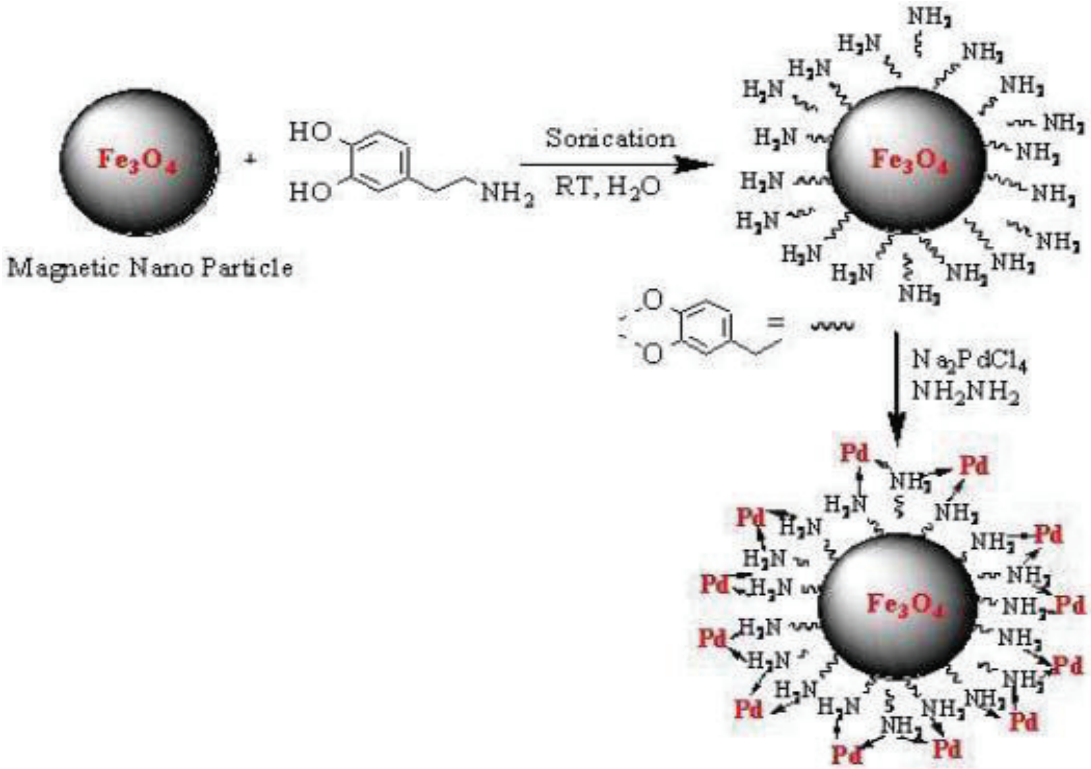
Scheme 8. Synthesis of magnetically separable hydroformylation catalyst.

❖ **Connon** prepared the magnetic nanoparticle-supported 4-N,N-dimethylaminopyridine analogue and successfully used it as a heterogenous catalyst for a range of useful synthetic transformations with excellent activity and recyclability(Scheme 9).The ease of recovery, as well as superb stability of the catalyst system, made it easily recyclable using an external magnet. The catalyst was used up to 30 times without any noticeable loss in activity.[34] Similarly, they prepared a chiral version of this catalyst and it was successfully used for an enantioselective acylation reaction.[35]



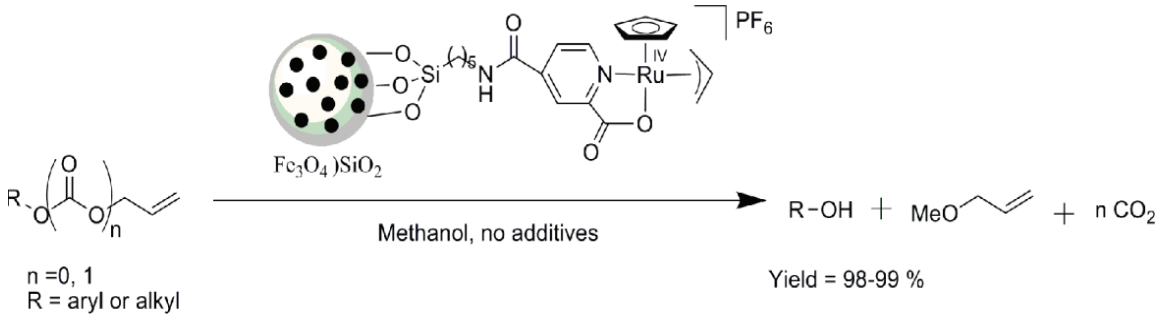
Scheme 9. Magnetically separable 4-*N*,*N*-dimethylaminopyridine as a catalyst.

- For the development of other metal-catalysts[36,37,38] including a nano-ferrite-supported Pd catalyst from inexpensive starting materials in water (Scheme 10).[39,40] This material catalyzed the oxidation of alcohols and olefins with high turnover numbers and excellent selectivity. The catalyst was able to be magnetically separated, which eliminated the requirement of its filtration,which was an additional sustainable attribute of this oxidation protocol.



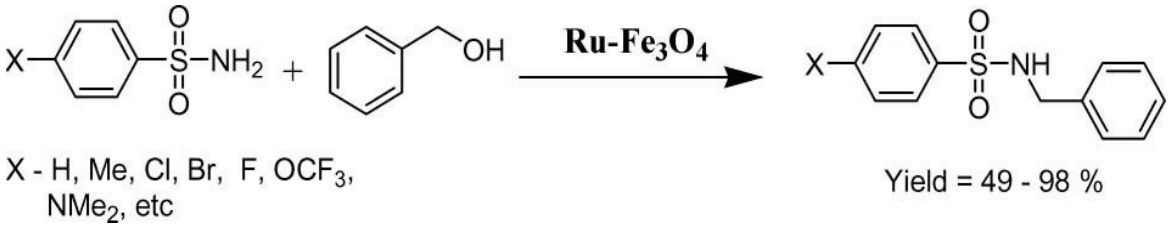
Scheme 10. Dopamine functionalized nano-ferrite Pd catalyst.

❖ **Kitamura and co-workers** prepared a deallylation catalyst by immobilization of [CpRu(η^3-C_3H_5)(2-pyridinecarboxylato] PF_6 on silica-coated nano-ferrite particles.[41] The obtained materials showed high saturation magnetization and levels of dispersibility with weak coercive forces.The catalyst was highly active for deallylation reactions (Scheme 11) and no extra additives were needed to complete the reaction. Only volatile allyl ethers were the co-products of the reaction. The catalyst was removed using an external magnet and reused, making the protocol economical.



Scheme 11. Magnetically separable deallylation catalyst

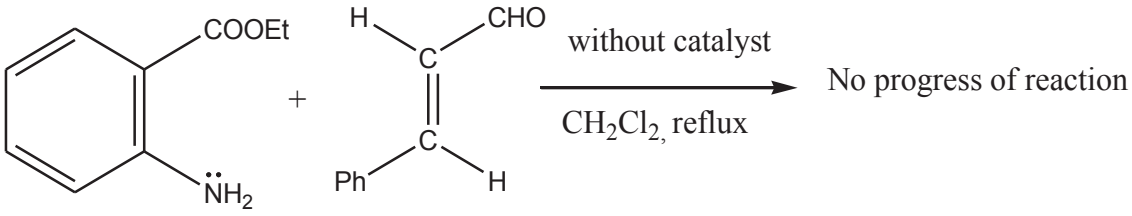
❖ **Beller *et al.*** reported magnetically separable nano-ferrite as a support for the development of Ru–Fe_3O_4 catalyst[42] and successfully demonstrated its catalytic prowess for the synthesis of a variety of sulfonamides with excellent yield (Scheme 12). Further, it was observed that only one equivalent of alcohol was needed to complete the reaction and the catalyst could be used several times, making the protocol green and sustainable.



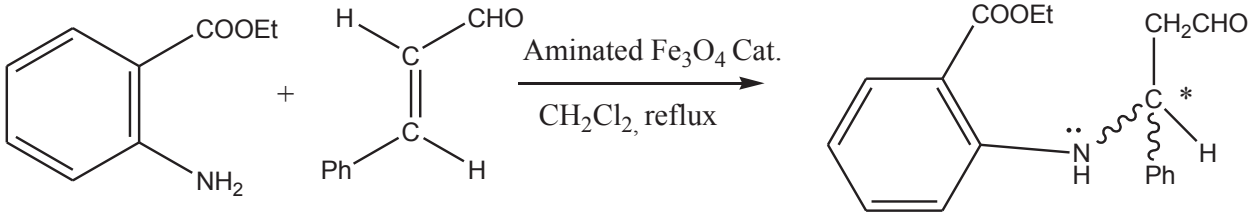
Scheme 12. Magnetically separable Ru catalyst for synthesis of sulfonamides

➢ Objectives

While working in our laboratory, when ethyl-2-aminobenzoate was reacted with cinnamaldehyde, no aza-Michael reaction took place even after refluxing for several hours. Since many reports were available for magnetite catalysed Michael addition reactions, we thought to use Fe_3O_4 nanoparticle as catalyst and to our great delight, the reaction was successful.



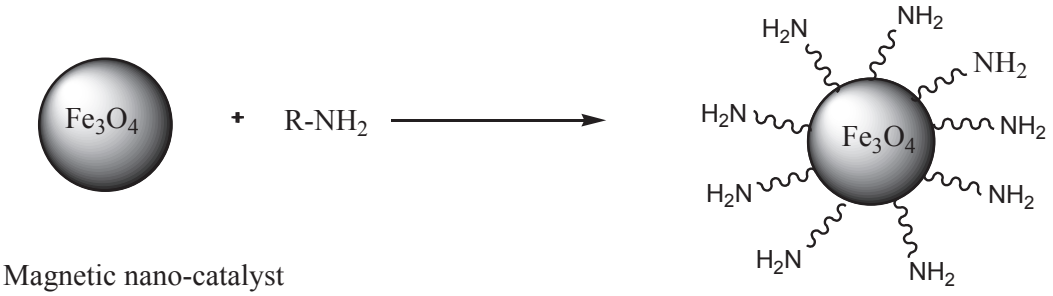
Ethyl-2-aminobenzoate Cinnamaldehyde



Ethyl-2-aminobenzoate Cinnamaldehyde Chiral adduct

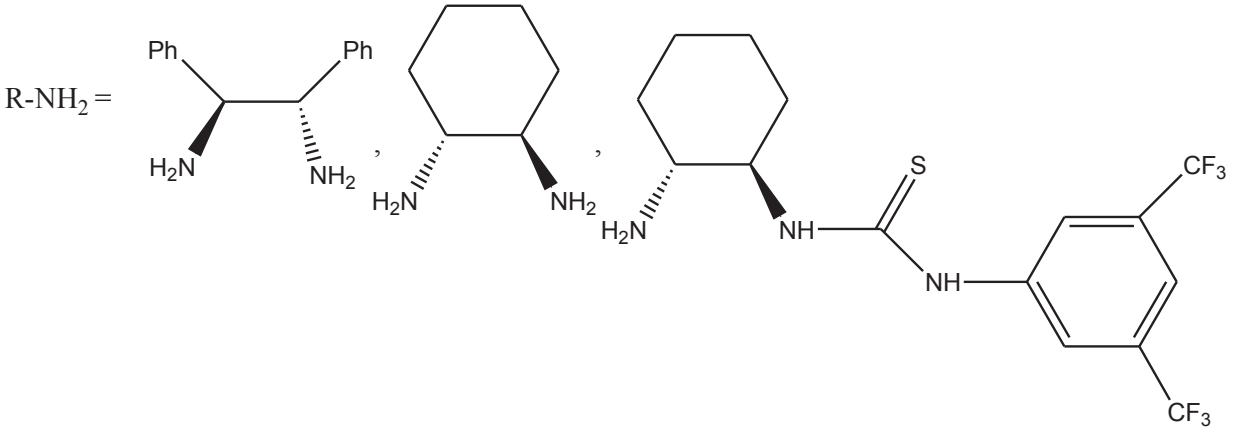
Moreover, it was found that the prepared nano-catalyst was not stable for longer hours so its coating with some substituted amines was also planned.

1) Preparation of amine coated magnetic nano-catalyst



Magnetic nano-catalyst

Amine coated magnetic nano-catalyst

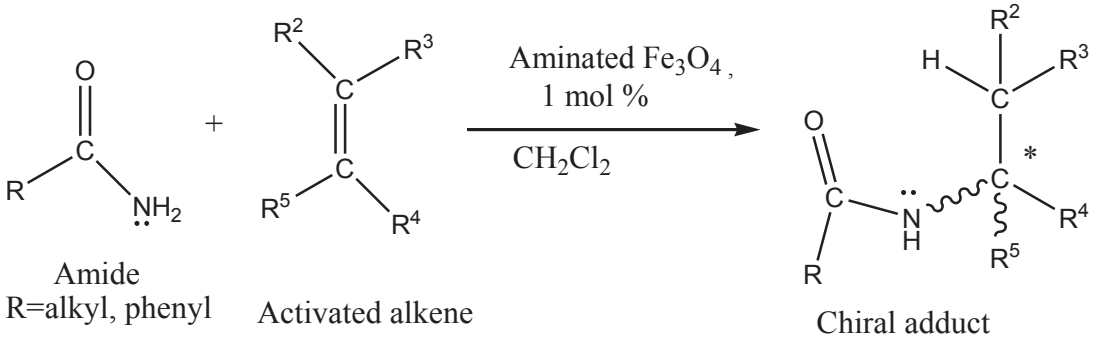


The methodology used for synthesis of the above catalyst will be done as reported in the paper below-

M. Mitra, Y. Nan, B. Nadi and M. Audrey "Cu(II) Galvanic reduction and deposition onto iron nano- and microparticles: resulting morphologies and growth mechanisms". *Pubs.acs.org/Langmuir*. **2015**, 31, 789-798.

2) Application of the above catalyst in the following reaction

❖ **Aza-Michael adition reaction**



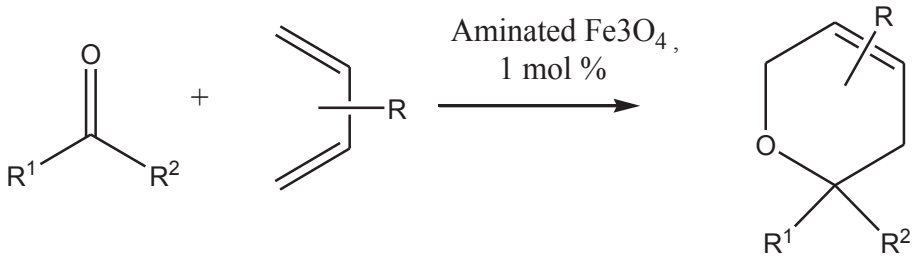
Amide
R=alkyl, phenyl

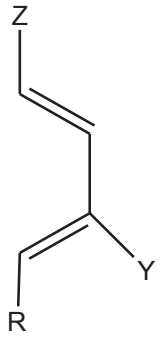
Activated alkene

Chiral adduct

S.No.	R	R^2	R^3	R^4	R^5
1	Alkyl,Phenyl	H	CHO	H	Methyl
2	Alkyl,Phenyl	Methyl	CN	H	Ethyl
3	Alkyl,Phenyl	Ethyl	NO_2	H	H
4	Alkyl,Phenyl	Metyl	CO	H	H

❖ **Hetero Diels Alder reaction**





R=alkyl,aryl
Y=not alkyl
Z=CO_2R, $CONR_2$ or COX^*
(X^*=Chiral auxilliary)

S.No.	R^1	R^2	R
1	Ph	H	H
2	Ph	Me	Me
3	p-Me-C_6H_4	H	OMe

➢ Methodology

1) Preparation of amine coated magnetic nano-catalyst

The methodology used for synthesis of the above catalyst will be done as reported in the paper below-

M. Mitra, Y. Nan, B. Nadi and M. Audrey "Cu(II) Galvanic reduction and deposition onto iron nano- and microparticles: resulting morphologies and growth mechanisms". Pubs.acs.org/Langmuir. 2015, **31**, 789-798.

2) Application of the above catalyst in aza-Michael addition reaction

The methodology used for application of the above catalyst will be done as reported in the paper below-

A.Klaus, T. Rajeswari, U.Naoto, T.Fujie and F.B.Carlos, III "Amine-catalysed Michael reactions of an aminoaldehyde derivative to nitroolefins"Tetrahydron Letters 2007, **48**, 693-696

Characterization of product

The products will be characterized on the basis of SEM, TEM, IR, ^{1}H NMR & ^{13}C NMR .

Facilities available at the place of work

- A well equipped research laboratory
- As we do not have facilities for the elemental analysis and NMR studies at the IIS university , the same will be availed at Malaviya National Institute of Technology and Therachem on payment basis.

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